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(54) Title: COMPRESSIVE STRENGTH IMPROVEMENT OF FIBERS BY MEANS OF RADIAL RESTRAINT

(57) Abstract

A filiform article comprises a fiber wrapped, fiber core impregnated with resin. Reinforcing fibers are organized into cores that contain at least one reinforcing fiber, but preferably contains a plurality of fibers. The core is surrounded by a sheath containing a wrapping fiber. The wrapping fiber is preferably wrapped around the core with tension. The core is impregnated with a flowable, hardenable resin preferably after the core is wrapped. The diameter of the filiform article is preferably no more than 1.5 mm. The filiforms may be prepegged according to known practices.

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COMPRESSIVE STRENGTH IMPROVEMENT OF FIBERS BY MEANS OF RADIAL RESTRAINT

The present invention relates to fibers and matrix composites which contain them.

Composites contain a matrix resin that contains and is supported by a reinforcing fiber. The reinforcing fiber is usually one with a high tensile strength and/or tensile modulus. Examples of reinforcing fibers include some carbon fibers, aramid fibers (commercially available under the trademark Kevlar™ from E.I. DuPont de Nemours & Co.); highly-oriented polyethylene fibers (commercially available under trademark Spectra™ from Allied-Signal Corp.); and polybenzazole fibers.

Fibers that have a high tensile strength typically have a relatively low compressive strength, and vice-versa. The compressive strength of fibers with high tensile strength is seldom more than 30 percent of tensile strength, and is frequently much less. They also frequently have a very low compressive strain-to-failure ratio, requiring little work to cause compressive failure in the fiber. The poor compressive

properties of reinforcing fibers has greatly reduced the usefulness of those fibers in matrix composites for many structural applications.

Many attempts have been made to improve the compressive strength of oriented polymer fibers. For instance, polymer within the fibers has been cross-linked as reported in Arnold, "Structural Modifications of Rigid-Rod Polymers," The Materials Science and Engineering of Rigid Rod Polymers 117, 121-22 (1989). However, those polymer-based methods have not yielded a fiber having a compressive strength at least 100 percent greater than the compressive strength of the uncross-linked fiber.

The patent of Antal et al., Reinforcement Structure, U.S. Patent 4,499,716 (February 19, 1985) teaches that compressive strength may be improved by wrapping a thick core of high tenacity fiber, which is typically solidified into a bar by impregnating with epoxy resin and curing prior to wrapping, with a helical wrapping of high tenacity yarn under very high tension, such that the core is under at least 0.1 percent radial compression. However, the structures taught in the patent are stiff and inflexible. Flexibility is desirable so that the fiber may be wrapped on a spool and shaped to conform to a desired shape before curing in a composite.

What is needed is a means to increase the compressive strength of a fiber or a matrix composite containing the fiber and/or increase the amount of work needed to cause compressive failure of a fiber or a matrix composite containing the fiber, while leaving the

the fiber sufficiently flexible enough to be drapable and handleable prior to curing in a composite.

One aspect of the present invention is a filiform article containing: (a) a core containing one or more essentially parallel core fibers; (b) a sheath containing one or more wrap fibers surrounding the core and covering at least 50 percent of the outer surface of the core; and (c) a hardenable resin that is flowable before it is hardened and is hardenable to provide a hardened resin having a compressive modulus of at least 50,000 psi, characterized in that:

(1) the core has an average diameter of no more than 0.8 mm and contains fibers whose compressive strength that is no more than 30 percent of their tensile strength;

(2) the wrap fibers place the core under radial compression of less than 0.1 percent; and

(3) the hardenable resin impregnates both the core and the sheath.

A second aspect of the present invention is a matrix composite containing (a) a plurality of supporting fibers whose compressive strength is no more than 30 percent of their tensile strength; and (b) at least one matrix polymer, which has a compressive modulus of at least 50,000 psi, characterized in that:

(1) the supporting fibers are organized into cores of essentially parallel fibers wrapped by a wrap fiber, wherein each core has an average diameter of no more than 0.8 mm, and the structure

of wrap and core fibers together have an average diameter of no more than 1.3 mm;

(2) the matrix resin is in contact with both the core fibers and the wrap fibers; and

(3) the matrix composite has a compressive strength of at least 20 MPa.

A third aspect of the present invention is a process comprising the steps of:

(1) winding a sheath fiber with a tension of at least 21 grams and no more than 1000 grams around the core having an average diameter of no more than 0.8 mm containing a plurality of fibers whose compressive strength is no more than 30 percent of their tensile strength, whereby a filiform article is formed; and

(2) impregnating the filiform article with a flowable resin, which is hardenable to form a hardened polymer having a compressive strength of at least 50,000 psi, such that the core and the fiber are both impregnated with the flowable resin.

The process of the present invention can be used to make filiform articles and prepregs of the present invention. Those filiform articles and prepregs are flexible enough to be drapable. The prepregs are useful for making composites, which can be shaped before curing to form useful structural materials. The composites preferably have a compressive strength at least 10 percent higher than the compressive strength of a similar composite made using the core fibers alone. They also preferably require substantially higher work

to cause compressive failure than do composites containing the unwrapped core alone.

The present invention uses a core containing a reinforcing fiber. The reinforcing fiber preferably has a tensile strength of at least 2 GPa, more preferably at least 3 GPa and most preferably at least 4 GPa. It preferably has a tensile modulus of at least 100 GPa and more preferably at least 200 GPa.

The compressive strength of the reinforcing fiber is no more than 30 percent of its tensile strength. It is usually les than 1 GPa, and may be less than 0.5 GPa or even les than 0.30 GPa. The polymer is preferably an aramid, a highly oriented polyethylene or a polybenzazole. It is more preferably an aramid or a polybenzazole and most preferably a polybenzazole. Suitable fibers are discussed more fully hereinafter.

Aramid fibers are known and commercially available. Exemplary suitable fibers are commercially available under the trademarks Kevlar™, Twaron™ and Technora™. The polymers in the fibers preferably contain primarily p-phenylene moieties linked by amide groups. Certain preferred polymers contain a mixture of m- and p-phenylene moieties linked by amide groups, but the most preferred polymers contain essentially no m-phenylene moieties. Aramid fibers are discussed in greater detail in 3 Kirk-Othmer Ency. Chem. Tech. (3rd Ed.), Aramid Fibers, 213 (J. Wiley & Sons 1978).

Oriented polyethylene fibers are also known and commercially available. Oriented polyethylene fibers are typically gel-spun, ultra-high molecular weight

polyethylene. Exemplary suitable fiber is commercially available under the trademark Spectra™ from Allied-Signal Co.

Polybenzazole polymers and processes to make fibers from them are also known. Polybenzazole polymers contain a plurality of mer units that comprise:

(1) an aromatic group (Ar); and

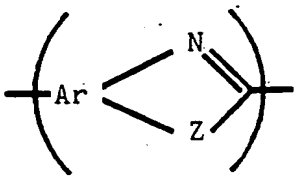
(2) a first azole ring fused with the aromatic group;

and preferably further comprise:

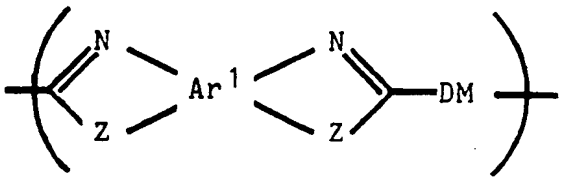
(3) a second azole ring fused with the first aromatic group; and

(4) a divalent organic moiety (DM) that does not interfere with the synthesis fabrication or use of the fiber bonded to the 2-carbon of the second azole ring.

Polybenzazole mer units are preferably represented by one of Formulae 1(a) or (b), and more preferably by Formula 1(b):



1(a) AB

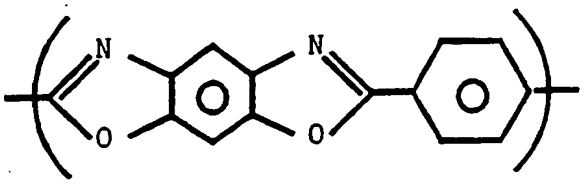


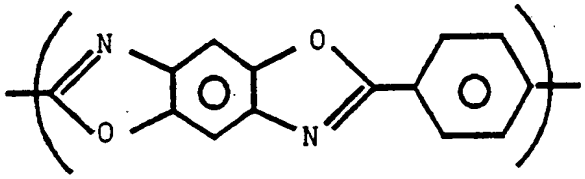
1(b) AA/BB

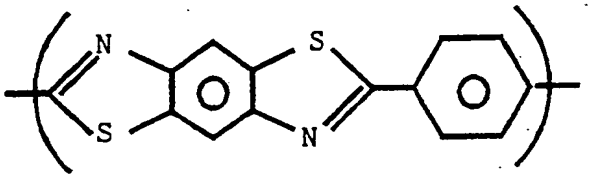
wherein each Ar represents an aromatic group; each Z represents -O-, -S- or -NR-, wherein each R is a hydrogen atom, a lower alkyl group or a phenylene moiety; and each DM represents a bond or divalent organic moiety as previously defined.

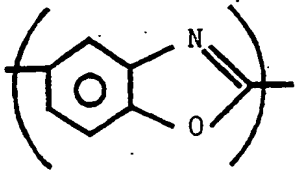
Each aromatic group (Ar) is preferably a carbocyclic group containing no more than 12 carbon atoms, and more preferably either a 1,3,4-phenylene moiety in the case of AB-polybenzazole (AB-PBZ: Formula 1(a)) or a 1,2,4,5-phenylene moiety in the case of AA/BB-polybenzazole (AA/BB-PBZ: Formula 1(b)). Each azole ring is preferably an oxazole or a thiazole ring (-Z- = -O- or -S-) and more preferably an oxazole ring (-Z- = -O-). Each DM is preferably an aromatic group and more preferably a 1,4-phenylene moiety. The preceding moieties are preferably chosen such that resulting polymer is a rigid rod polymer or a semi-rigid polymer and are more preferably chosen such that the resulting polymer is a rigid rod polymer. Examples of highly preferred mer units are represented by Formulae 2(a)-(e):

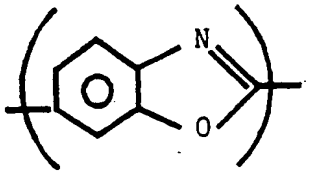
2

(a)  ,

(b)  ,

(c)  ,

(d)  , and

(e)  .

The polybenzazole polymer may be a polybenzazole "homopolymer," consisting essentially of a single repeated of mer unit as described in U.S. Patent 4,533,693 at Columns 9 to 45; or may be a random or

block "copolymer" such as those described in U.S. Patent 4,533,693 at Columns 45-81 and in Harris et al., Copolymers Containing Polybenzoxazole, Polybenzothiazole and Polybenzimidazole Moieties, International Application No. PCT/US89/04464 (filed October 6, 1989), International Publication No. WO 90/03995 (published April 19, 1990). The polymer is preferably a "homopolymer". It more preferably forms a liquid crystalline solution when dissolved at a suitable concentration in a solvent acid, such as polyphosphoric acid and/or methanesulfonic acid, and/or coagulates from solvent acid to form a crystalline or semicrystalline coagulated fiber.

The polybenzazole polymer preferably should have sufficient molecular weight to form a spinnable dope solution. Its molecular weight is preferably at least 5000; more preferably at least 10,000; and most preferably at least 25,000. For poly-(para-phenylene-cis-benzobis-oxazole) (cis-PBO) the intrinsic viscosity of the polymer in methanesulfonic acid at 25°C and 0.05 g/dL concentration is preferably at least 10 dL/g, more preferably at least 20 dL/g and most preferably at least 30 dL/g. It is preferably no more than 50 dL/g.

The polybenzazole polymers may be synthesized by reaction of suitable monomers in dehydrating acid solutions, such as polyphosphoric acid and/or a mixture of methanesulfonic acid and P_2O_5, with vigorous agitation under nitrogen atmosphere. Reaction temperatures are typically between 75°C and 220°C, and are usually increased in a step-wise manner. The resulting dope is then spun and drawn into a suitable coagulant bath by ordinary dry-jet wet-spinning

techniques to form fibers. Synthesis of suitable polybenzazole polymer and fiber spinning are described in numerous references, such as in U.S. Patents 4,263,245; 4,533,693 and 4,776,678; in PCT International Publication No. WO 90/03995 (published April 19, 1990); and in Ledbetter et al., "An Integrated Laboratory Process for Preparing Rigid Rod Fibers from the Monomers," The Materials Science & Engineering of Rigid Rod Polymers 253 (Materials Research Society 1989).

The spun polybenzazole fiber may be exposed to brief high temperature under tension ("heat treatment" or "heat setting") to improve tensile strength and/or modulus, such as is described in U.S. Patent 4,544,119, which is incorporated herein by reference. Heat treatment may be for any period of time from a few seconds to 30 minutes, and at a temperature between 300°C and 700°C, inclusive. Of course, longer residence time is ordinarily desirable at lower temperatures and shorter residence time at higher temperatures.

The reinforcing fibers in the present invention are organized into cores that contain at least one reinforcing fiber. The core may contain a single fiber, but preferably contains a plurality of fibers. The core fibers are preferably parallel with each other. More preferably, at least some of the fibers in the core are not substantially twisted but extend essentially parallel to the long axis of the filiform article. The core may contain two or more types of fiber, such as a mixture of aramid fibers and polybenzazole fibers.

The maximum and minimum size of the core are governed primarily by practical considerations. A core

having too small an average diameter is undesirable for at least two reasons. First, a core containing only one fiber is so thin that it is difficult to sheath by wrapping with a wrap fiber unless the wrap fiber is very flexible. Second, a very thin core is more likely to have a high ratio of sheath to core fiber. It is desirable to minimize the ratio of sheath to core fiber in order to obtain the best composite properties. On the other hand, a core having too large an average diameter is also undesirable because a thicker core is ordinarily substantially less flexible than a thin core.

The core has an average diameter of no more than 0.8 mm. The average diameter is preferably no more than 0.6 mm, more preferably no more than 0.5 mm and most preferably no more than 0.4 mm. The average diameter of the core is preferably at least 0.05 mm and more preferably at least 0.1 mm. When the fiber is an aramid fiber such as Kevlar™ fiber, then the core preferably has a denier no higher than 3000, more preferably no higher than 2500 and most preferably no higher than 1500; and it preferably has a denier of at least 200, more preferably at least 500 and most preferably at least 1000.

The core is surrounded by a sheath containing a wrapping fiber that surrounds the core. The wrapping fiber should be flexible enough to wrap securely around the core without substantial damage. The wrapping fiber preferably has a high glass transition temperature and sufficient thermal stability to permit its use throughout most of the temperature range in which the core fiber is useful. Suitable wrapping fibers may contain, for example, polybenzazole, aramid, nylon,

polyester, polypropylene, or polyethylene. Preferred wrapping materials are polybenzazole fiber and aramid fiber. The polybenzazole is preferably not a rigid rod polybenzazole, but is preferably an AB-polybenzazole or a flexible coil AA/BB-polybenzazole polymer.

The wrapping fiber may be wrapped around the core using a number of known devices. Examples of processes for wrapping fibers around fibers, and the products of those processes, are described in numerous references, such as U.S. Patents 3,495.646; 3.556,922; 3,644,866; 4,269,024; 4,272,950; 4,299,884; 4,384,449; 4,499,716; and 4,861,575, which are incorporated herein by reference.

If the core is very thin, such as a single fiber, then it is often difficult to wrap the core with a solidified fiber without damaging the core. Instead, the core may be wrapped with a fiber made of flowable and hardenable material, such as wrapping a strand of polybenzazole-containing acid dope or an aramid--containing acid dope or a molten nylon around the core. The flowable wrapping is then solidified, by coagulating in the case of a dope or by cooling in the case of a molten polymer. The flowable wrapping should be viscous enough to substantially hold its shape until coagulated. The flowable wrapping is preferably a polybenzazole dope.

The sheath should be thick enough to provide radially restraining pressure without breaking. However, the sheath is preferably as thin as possible for two reasons. First, thicker sheaths add to the overall thickness of the filiform article. Thicker

filiform articles are less flexible, and have poorer drapability and handleability. Second, higher composite compressive and tensile strengths are realized when the filiform article contains a high ratio of core fiber to sheath. It is theorized that the axial strength of the filiform article, both in tension and in compression, comes primarily from the core, rather than from the sheath. If the sheath occupies a large part of the volume allowed for the filiform article in a composite, then the volume must contain an equivalently smaller amount of core fiber. By making the sheath as thin as practical, the amount of core fiber, and the strength of the resulting composite, can be maximized.

Actual thicknesses are governed primarily by practical considerations of wrapping fiber strength and flexibility. The sheath is preferably no more than 0.2 mm thick, more preferably no more than 0.15 mm and most preferably no more than 0.1 mm thick. A sheath containing a wrapping fiber may have one, two or more layers of wrapping, but preferably contains no more than two layers and more preferably no more than one layer.

The wrap fiber need not cover 100 percent of the outer surface of the core. The wrapping fiber preferably covers at least 70 percent of the core surface, more preferably at least 90 percent of the core surface, and most preferably 100 percent of the core surface.

The wrapping fiber is preferably wrapped around the core with tension. Preferably, the wrapping mechanism used to wrap the core has a tension producing means, such as a brake or clutch for the wrapping fiber.

If it does not, some tension may be generated by wrapping at high speeds in hollow core spindle equipment, such as Leesona Coverspun™ equipment. The speed of wrapping when the wrapping equipment does not contain a tensioning device is preferably at least 15,000 wraps per minute and more preferably at least 30,000 wraps per minute.

The tension on the wrapping fiber is preferably at least 20 grams, more preferably at least 50 grams and most preferably at least 75 grams. Very high tension is neither necessary nor desirable. Wrapping the core under high tension twists and deforms the core unless the core is itself under high tension, and a core under high tension must be undesirably thick to avoid breaking. The tension of the wrapping is preferably no more than 1000 grams, more preferably no more than 500 grams and most preferably no more than 260 grams. The foregoing tensions are suitable for wrapping fibers having a diameter about equivalent to that of a 200 denier Kevlar™ 49 aramid fiber. Persons of ordinary skill can adjust those tensions appropriately for other fibers to obtain an essentially equivalent radial restraining pressure. Tensions sufficient to compress the radial diameter of the core by 0.1 percent are undesirable and should be avoided.

The core is impregnated with a flowable, hardenable resin prior to wrapping and subsequently hardening the matrix resin. The resin is preferably impregnated into the core after the core is wrapped. The flowable, hardenable resin may be a molten thermoplastic polymer, such as poly(aromatic ether ketone), poly(aromatic ether sulfone) and

poly(etherimide). The flowable, hardenable resin is preferably a thermosetting resin, such as epoxy resins, polycyanate resins, phenolic resins, butadiene resins, vinyl ester resins and polyimides. The thermosetting resin is preferably an epoxy resin or a polycyanate resin. The flowable, hardenable resin preferably has a compressive modulus after curing of at least 50,000 psi. more preferably at least 100,000 psi, and most preferably at least 250,000 psi.

The flowable, hardenable resin should not be fully cured prior to wrapping, but may be partially cured as long as the filiform article remains flexible. The wrapped filiform article is much stiffer and less handleable after the resin is cured. Therefore, the resin should not be fully cured until after the sheath is applied to the core, and preferably not until a matrix composite containing the filiform article is cured.

The diameter of the filiform article, containing both sheath and core, is preferably small enough that the filiform article remains flexible, so that it is drapable and handleable. The diameter is preferably no more than 1.5 mm, more preferably no more than 0.8 mm and most preferably no more than 0.6 mm. The minimum diameter of the filiform article is governed primarily by practical considerations, such as the size of core fibers and the flexibility of wrapping fibers. The filiform article preferably has a diameter of at least 0.1 mm and more preferably at least 0.3 mm.

The filiform article may be prepregged according to known practices by impregnating the sheath.

and the core if it is not previously impregnated. with a flowable, hardenable resin. The flowable, hardenable resin has the same definition and preferred embodiments as the resin discussed for impregnating the core and is preferably similar to the resin which impregnates the core. The core is preferably impregnated before it is sheathed, and the sheath of the filiform article is preferably impregnated with resin in a separate step while the sheath is added to the core or afterwards. If no resin is added to the core before it is sheathed, subsequent prepregging may not completely impregnate the core, and the resulting composite may have lower compressive properties.

The resulting prepreg should contain sufficient flowable and hardenable matrix resin to bend the fibers together and so that the prepreg is curable with a plurality of other prepregs to form a matrix composite. The prepreg preferably contains enough matrix resin to minimize voids in the filiform article. In the present invention, it is desirable to maximize the volume percent of the prepreg and composite that is occupied by core fibers, while adequately filling voids and maintaining radial pressure on the core fibers to maximize compressive properties. Prepregs and the resulting matrix composites typically contain 25 to 60 volume percent matrix resin and 40 to 75 volume percent fibers or filiform articles. The prepreg or composite more preferably contains at least 60 volume percent filiform articles. It preferably contains no more than 20 volume percent void, more preferably no more than 10 volume percent, more highly preferably no more than 5 percent and most preferably no more than 2 volume percent.

Prepregging and formation of matrix composites are described in numerous general references, such as Kirk-Othmer Ency. Chem. Tech. - Supplement, Composites, High Performance, 260-80 (J. Wiley & Sons 1984), which is incorporated herein by reference. The uncured prepregs may then be laminated, draped over molds and otherwise shaped. The shaped prepregs are hardened by curing a thermosetting hardenable resin or cooling a thermoplastic one, in order to form a shaped article. The shaped article may be further machined, and is useful as a structural or electronics material.

An improvement in compressive strength in the filiform article does not necessarily translate directly into a proportional improvement in composite properties. The core fibers do not make up 100 percent of a composite even using unsheathed fibers, and the sheathing reduces the volume of core fibers in the matrix even further. However, the matrix composite made using the filiform article preferably has a compressive strength at least 10 percent higher than that using an unsheathed fiber. The improvement in compressive strength is more preferably at least 20 percent, more highly preferably at least 50 percent, and most preferably at least 90 percent.

When the core fiber is polybenzazole polymer, the compressive strength of a composite containing the filiform article is preferably at least 22 kpsi (151 MPa), more preferably at least 30 kpsi (200 MPa) and most preferably at least 35 kpsi (240 MPa). When the core fiber is an aramid, the compressive strength of a composite containing the filiform article is preferably

at least 30 kpsi (207 MPa), more preferably at least 35 kpsi (240 MPa), and most preferably at least 40 kpsi (275 MPa). When the core fiber is an oriented polyethylene, the compressive strength of a composite containing the filiform article is preferably at least 16 kpsi (110 MPa) and more preferably at least 20 kpsi (138 MPa).

The filiform articles, and composites that contain them, can preferably withstand much greater compressive strain before compressive failure occurs than can unsheathed core fibers, so that the work required to cause compressive failure is increased. The strain to compressive failure in a composite containing filiform articles having an aramid core or polybenzazole is preferably at least 10 percent, more preferably at least 15 percent and most preferably at least 19 percent.

The following Examples are for illustrative purposes only, and are not to be taken as limiting either the Specification or the claims. Unless otherwise indicated, all parts and percentages are by weight.

Throughout the examples, fiber and composite compressive strength is measured by a minicomposite measuring technique, which is a small scale adaptation of ASTM D-3410-82 and, in our experience, provides generally equivalent results with that ASTM test. A bundle of parallel fibers or filiform articles is impregnated with Tactix® 123 epoxy resin and Tactix® Hardener H31 curing agent in a weight ratio of 100:17 and laid up in uniaxial fashion in a Teflon™ coated

mold. The mold is filled with the same epoxy resin and hardener in the same proportions. The epoxy resin is cure to provide a minicomposite. The mold provides a test section containing the bundles and cured epoxy resin, said test section having a cross-sectional area of 0.062 inches by 0.125 inches and a length in the axial direction of 0.19 inches. The fiber bundles extend beyond each end of the test section into epoxy tabs located at each end of the test section. The ends of the tabs are cut planar, parallel to each other and perpendicular to the test section, using a diamond saw. The specimen is mounted on an Instron™ testing machine and compressed until failure occurs. The stress and strain to failure is recorded. The composite compressive strength is derived by dividing the stress at failure by the cross-sectional area of the test section.

Example 1 - Aramid Core Containing No Resin Wrapped with Aramid Fiber

A wrapping mechanism is constructed having a wrapping element from an American Volkmann Model No. VTS-05-0 twister mounted in a centrifuge case and driven by a centrifuge motor. The wrapping mechanism has an Accutense™ clutch mechanism model No. 250, manufactured by Textrol, Inc., to add tension to the wrapping fiber before it enters the wrapping element.

A core containing parallel fibers of Kevlar™ 49 aramid fiber having the denier set out in Table 1 (Core Denier) is wrapped with fibers of Kevlar™ 49 having the denier set out in Table 1 (Wrap Denier) to form a filiform article having a total denier as set out in

Table 1 (Total Denier). The wrapping speed is 7000 wraps per minute, and the wrapping coverage is 100 percent.

The wrapped fiber is impregnated again with the epoxy resin and hardener and tested for compressive strength as previously described. The testing results are set out in Table 1. The term "No. Bundle in Composite" refers to the total number of prepregged filiform articles in the test section of each specimen. The term "Total Test Denier" refers to the total denier of wrapped filiform articles contained in the minicomposite. The term "Total Core Denier" refers to the total denier of core fibers contained in the minicomposite. The term "Load to Break" refers to the compressive load on the minicomposite when compressive failure occurs. The term "Strain to Break" refers to the compressive strain of the minicomposite when compressive failure occurs. The term "Avg Composite Compress. Strength" refers to the average compressive strength calculated for this portion in the minicomposite.

TABLE 1

Sample	Core Denier	Wrap Denier	Total Denier	No. Bundles in Composite	Total Test Denier	Total Core Denier	Load to Break (g)	Strain to Break (%)	Avg. Composite Compress. Strength (kpsi/MPa)
C-1[1]	1140	0	1140	26	29600	29600	225	3.4	30/207
1(A)	200	200	1060	25	26500	5000	248	19.6	32/220
1(B)	380	200	1320	15	19800	5700	224	19.9	30/207
1(C)	580	200	1670	16	26700	9280	232	17.3	32/220
1(D)	760	200	1970	14	27600	10600	250	18.2	32/220
1(E)	960	200	2170	13	28200	12500	263	17.2	31/214
1(F)	1140	200	2400	12	28800	13700	243	15.8	33/228

[1] - comparative example

Example 2 - Aramid Core Impregnated with Epoxy Resin Prior to Wrap

The process of Example 1 is repeated, except that the core is impregnated with Tactix® 123 epoxy resin and Tactix® Hardener H31 curing agent prior to wrapping. The variables and results are set out in Table 2.

TABLE 2

Sample	Core Denier	Wrap Denier	Total Denier	No. Bundles in Composite	Total Prepreg Denier	Total Core Denier	Load to Break (lbs)	Strain to Break (%)	Avg. Composite Compress. Strength (kpsi/MPa)
C-1[1]	1140	0	1140	26	29600	29600	225	3.4	30/207
2(A)	380	200	1320	15	19800	5700	230	19	30/207
2(B)	580	200	1670	16	26700	9280	291	19.2	38/262
2(C)	760	200	1970	14	27600	10600	261	18.1	33/228
2(D)	960	200	2170	13	28200	12500	257	15.9	31/214
2(E)	1140	200	2400	12	28800	13700	299	18.1	39/269

[1] - comparative example

Example 3 - Variable Wrap Tension

The procedure set out in Example 2, Sample 2(E) is repeated except as follows:

The clutch mechanism is calibrated to determine the approximate tension at the wrap, in grams, of the wrap fiber which is generated by placing a particular DC voltage across the clutch and reading the tension with a Checkline™ tensiometer (1) just after the line leaves the clutch while the wrapping equipment is operating, and (2) just past the wrapping point while the wrapping equipment is stationary. The first measurement does not include friction from the equipment and is lower than the actual wrap tension. The second measurement include friction from equipment which is not in contact with the fiber when the wrapping equipment is in motion, and is higher than the actual wrap tension. Actual wrap tension is taken as being between the two. The results are set out in Table 3(A):

Table 3(A)

Voltage	Tension (g)
10.0	21-80
12.5	25-94
15.0	27-104
17.5	33-121
20.0	36-149
22.5	43-164
25.0	55-183
27.5	63-207
30.0	73-258

The wrapping and testing of 1140 denier aramid core at variable tensions is repeated as described in Table 3(B).

TABLE 3(B)

Sample	Wrap Denier	Total Denier	No. Bundles in Composite	Total Test Denier	Total Core Denier	Wrap Tension Voltage	Load to Break (lbs)	Strain to Break (%)	Avg. Composite Compress. Strength (kpsi/MPa)
C-2[1]	0	2280	13	29600	29600	--	203	4.5	28/193
3(A)	200	2330	13	30300	14800	7.5	249	13.2	34/235
3(B)	200	2330	13	30300	14800	15	273	14.9	38/262
3(C)	200	2310	13	30000	14800	20	253	12.7	34/235
3(D)	200	2290	13	29800	14800	25	279	15.2	38/262
3(E)	55	1770	17	30100	19400	18	262	13.6	37/255
3(F)	55	1760	18	31700	20500	20	278	13.5	40/276
3(G)	55	1770	17	30100	19400	23	266	14.3	38/262
3(H)	200	2500	13	32500	14800	14	335	16.6	44/303

[1] Comparative example using 2280 denier Kevlar-49

Example 4 - Oriented Polyethylene Core Impregnated with Epoxy Resin Prior to Wrap

The process of Example 2 is repeated using Spectra™ polyethylene fibers as the core and either 66 denier monofilament nylon or 10 strand 7 denier multifilament nylon as the wrapping fiber. The variables and results are set out in Table 4.

Example 5

The process of Example 3 is repeated using a 1300 denier polybenzoxazole fiber core and a 200 denier Kevlar™49 aramid fiber wrap. The wrap fiber clutch is set at 14 volts. The tension on the core is 140-158 g. The average denier of the wrapped fiber is 2680 denier.

A composite sample is prepared having 12 bundles of wrapped fiber. The core denier in the composite is 15,600 and the total denier of wrapped fiber in the composite is 32,300. A comparative composite that contains 25 bundles of unwrapped 1300 denier PBO (total denier 32,500) is prepared. The wrapped PBO composite has a compressive strength of 35 kpsi (240 MPa) and a strain-to-break of 22 percent. The unwrapped PBO composite has a compressive strength of 18 kpsi (125 MPa) and a strain-to-break of 5.7 percent.

TABLE 4

Sample	Core Denier	Wrap Denier	Linear rate of Core in wrapper (fpm)	No. Bundles in Composite	Load to Break (g)	Strain to Break (%)	Energy to Break (in.-lbs.)	Avg. Composite Compress. Strength (kpsi/MPa)
C-2[1]	650	0	-	20	30	5.5	0.25	11/76
6(A)	650	66	16	18	140	27.4	*	16/110
6(B)	650	66	16	18	156	26.2	5.51	19/131
6(C)	650	66	10	8	178	30.1	6.91	21/145
6(D)	650	71	16	23	83	10.2	1.03	11/76

[1] - comparative example

CLAIMS

1. A filiform article containing: (a) a core containing one or more essentially parallel core fibers: (b) a sheath containing one or more wrap fibers surrounding the core and covering at least 50 percent of the outer surface of the core; and (c) a hardenable resin that is flowable before it is hardened and is hardenable to provide a hardened resin having a compressive modulus of at least 50,000 psi, characterized in that:

(1) the core has an average diameter of no more than 0.8 mm and contains fibers whose compressive strength that is no more than 30 percent of their tensile strength;

(2) the wrap fibers place the core under radial compression of less than 0.1 percent; and

(3) the hardenable resin impregnates both the core and the sheath.

2. A matrix composite containing (a) a plurality of supporting fibers whose compressive strength is no more than 30 percent of their tensile strength; and (b) at least one matrix polymer, which has a compressive modulus of at least 50,000 psi, characterized in that:

(1) the supporting fibers are organized into cores of essentially parallel fibers wrapped by a wrap fiber, wherein each core has an average diameter of no more than 0.8 mm, and the structure of wrap and core fibers together have an average diameter of no more than 1.3 mm;

(2) the matrix resin is in contact with both the core fibers and the wrap fibers; and

(3) the matrix composite has a compressive strength of at least 20 MPa.

3. A process comprising the steps of:

(1) winding a sheath fiber with a tension of at least 10 grams and no more than 1000 grams around the core having an average diameter of no more than 0.8 mm containing a plurality of fibers whose compressive strength is no more than 30 percent of their tensile strength, whereby a filiform article is formed; and

(2) impregnating the filiform article with a flowable resin, which is hardenable to form a hardened polymer having a compressive strength of at least 50,000 psi, such that the core and the fiber are both impregnated with the flowable resin.

4. The process as described in Claim 3 which further comprises the steps of:

(3) laying up the impregnated filiform articles in the form of a selected shaped article; and

(4) hardening the flowable resin to form a matrix composite.

5. The invention as described in any one of the preceding Claims wherein the fibers in the core contain a polybenzazole polymer or an aramid polymer or an oriented polyethylene fiber.

6. The invention as described in any one of the preceding Claims wherein the hardenable resin is an epoxy resin or a polycyanate resin.

7. The invention as described in any one of Claims 1, 2, 4, 5 or 6 wherein the fiber wrapped around the core has a tension of at least 21 grams and no more than 1000 grams.

8. The invention as described in any one of Claims 2-7 wherein the core is under a radial compression of less than 0.1 percent.

9. The invention as described in any one of the preceding Claims wherein the product contains between 30 and 50 weight percent hardenable matrix resin.

10. The invention as described in any one of the preceding Claims wherein the wrap fiber covers at least 90 percent of the surface of the core.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/05407

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5) : B65H 81/06; D02G 3/36

U.S. CL. : 57/210, 232, 250, 295; 428/373, 377, 378, 394; 156/172, 180, 181

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
U.S.	57/210, 232, 250, 295; 428/373, 377, 378, 394; 156/172, 180, 181

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
Y	US, A, 4,499,716 (ANTAL) 19 FEBRUARY 1985. See the entire document.	1-5
Y	US, A, 4,272,950 (BOMPARD) 16 JUNE 1981. See the entire document.	1-5
Y	US, A, 4,265,981 (CAMPBELL) 05 MAY 1981. See columns 1, 2 and the claims.	2, 5

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
13 SEPTEMBER 1991	23 OCT 1991
International Searching Authority	**Signature of Authorized Officer**
ISA/US	Christopher Brown